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SUBSURFACE PROTECTION AND REMEDIATION DIVISION
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June 17, 1998

OFFICE OF
RESEARCH AND DEVELOPMENT

MEMORANDUM

SUBJECT: Technical Review Comments on Natural Attenuation at the Old City of York Landfill Superfund Site, York County, Pennsylvania (98-R03-011)

FROM: David S. Burden, Ph.D., Director
Technology Support Center

TO: John Banks
Remedial Project Manager
U.S. EPA - Region 3 (3HS22)

The following comments are in response to your request for technical assistance at the Old City of York Landfill Superfund Site, York County, Pennsylvania. Specifically, you ask for review of the potential for natural attenuation of ground-water contamination at the site. Your original request ask us to focus on three issues. The first issue, concerning an opinion regarding the installation of an additional monitoring well between the Boser well and the MW-E/MW-6 well pair, near Area #3 of the site was addressed in a memorandum dated June 11, 1999. This memorandum addresses the remaining two issues:

- An opinion on the viability of using natural attenuation at the site in lieu of the current pump and treat, and
- A recommendation for the minimum number of geochemical parameters to be monitored and the minimum data set which would be required for this site to complete a natural attenuation study.

The documents reviewed included (1) the ground-water analytical results (tables), (2) *The Monitored Natural Attenuation Evaluation Work Plan*, prepared by RUST, dated June 1998, and (3) the *Record of Decision*, dated September 1991. The review was conducted by Dr. Ann Azadpour of the Dynamac Corporation, an off-site contractor supporting EPA's Technology Support Center in Ada, OK. I have reviewed her comments and concur with them.

In general, on the positive side, the authors of the Work Plan unquestionably understand the processes involved in natural attenuation and present their case very clearly with a well written document. They have dealt with the myriad of complex issues one necessarily faces in attempting to persuade environmental authorities that natural attenuation is one of the most

feasible remedial alternative for this site. The issues of remedial objectives, available remedial action technologies, ARARs, exposure, and risk assessment have been professionally considered. On a slightly more negative note, some of their conclusions often appear self serving and, at times, are not to be strongly supported by the evidence.

All attempts to promote natural attenuation, or any other remedial alternative, should be strongly based on a through understanding of site characteristics including the hydrogeologic setting, the type and distribution of contaminants of concern, and the processes involved in the reduction of the mass of those contaminants to an acceptable level.

Although the authors have demonstrated their awareness of the various processes governing reduction in mass and/or concentration of the contaminants of concern at this site, the repeated assurance that ..."a review of historic ground-water data indicates that natural attenuation is occurring at the Site..." is misleading. It is noted that it is the ***rate*** and not the occurrence of the natural processes that are pertinent in remedial projects. Furthermore, the EPA directive realizes the role of biodegradation as the primary route of removal for the chlorinated solvents. It is our opinion that adequate response to these issues were not addressed in the current Work Plan.

The document stated that (Page 1-1) this Work Plan will seek to determine which natural attenuation mechanisms (i.e., dispersion, dilution, sorption, biodegradation, etc.) is predominant and whether the rate of natural attenuation is appropriate to meet remedial action objectives. It is noted that the Work Plan does not meet these stated objectives. In fact, a complete lack of information relating to the abiotic processes at this site is evident. Also, it seems that the fundamental requirements for biotic degradation may not be in place as indicated by high oxygen content and compounded by low concentrations of dissolved organic carbon.

The Work Plan is very brief in comparison to the plethora of similar documents which we routinely review. For example, it does not provide a comprehensive site characterization which must serve as the foundation of any remediation technology. Not only are the interrelationships between the various biotic and abiotic components of the system not addressed, a work plan should lead to development of a conceptual or mathematical model from which the final design and operation can be derived. It is also important to develop a statistical plan that, in the end, will provide the results of the investigation with irrefutable validity.

A thorough demonstration of natural attenuation processes requires monitoring for parameters that are sensitive in time and space. Therefore, it would be premature to assume that preforming two rounds of natural attenuation monitoring for ground water (Page 1-1) may adequately describe this complex system.

In lieu of the three lines of evidence for natural attenuation presented in Section 1.1, it is suggested that there are at least four basic conditions which must be present to confirm that natural attenuation processes are taking place. These include, but are probably not limited to:

1. The points of sampling must be on flow lines from the source of contamination or an up gradient point of observation.
2. There must be a reduction in contaminant mass.
3. Site geochemistry must assure that conditions are right for reduction such as the presence of electron acceptors, state of redox, etc.
4. Daughter products of contaminants must be present, perhaps with indicators of mineralization.

It would appear at this juncture, that the primary effort should focus on the development of a conceptual model that adequately describes the geochemical system. It is also extremely important that adequate statistical considerations be envisioned at this early stage to evaluate long term monitoring data.

This may seem to be premature at this point, however, experience has shown that natural attenuation assessments are considerably more time sensitive than usually anticipated. It is not only dependent on the length of study, but the frequency as well. For example, in order to demonstrate that the processes of natural attenuation are occurring, and make an estimate of the rate of attenuation, it is necessary to develop a statistical evaluation of trends (least squares) or changes in concentrations over time (analysis of means). Both of these tests are functions of variance of data and the degrees of freedom. In these cases the degrees of freedom are N-2. The point is that only protracted time measurements at a reasonable frequency will provide the proof of a statistical correlation of time and concentration by obtaining a correlation coefficient of 0.8 or higher. These types of studies often lead to more lengthy monitoring periods than are originally anticipated.

It would appear that selling natural attenuation at this site based on the apparent reduction in contaminant mass is not appropriate. A more feasible argument would be that the concentrations of contaminants of concern (COCs) are relatively low with the higher concentrations being confined to relatively isolated areas located in the region of Area 1 and the northeast section of Area 3, the areas of contamination are fairly well defined along with their probable source(s), conditions seem favorable for the processes of natural attenuation to be effective, and there is time to make a technically defensive determination that these processes are in fact ongoing. As appropriately pointed out in the document, if natural attenuation proves not to be effective, a contingency plan (restoration of pump and treat) would be put into effect to enhance remediation.

The following specific comments are offered in a bullet format for the sake of simplicity:

- Page 1-3, 1st Paragraph. The performance of the microbiological analysis as suggested in the document seems to be an unwarranted effort. It is established that the presence of microorganisms do not necessarily equate to biodegradation of the COCs. The abundance of microbial community at a landfill site is not

surprising. What seems to be puzzling is a low density of the bacterial population at many monitoring locations at this site. If the intent is to indicate that the microbial community are capable of COCs degradation, a heterotrophic plate count may not generate useful information since it will only indicate the total microbial count. Determination of FAME may reveal more information.

On the contrary, the total number of microorganisms counted indicated that the abundance of microbial population may not be adequate. Similarly, as evidenced in Table 2-2, concentrations of intermediatory metabolites produced during microbial metabolism of organic compounds are significantly low and below the detection limits.

- It is suggested that an in-depth study of the existing data be made to assure its quality and perhaps remove information that could bring its validity into question. For example, some of the comments made in the *remarks* column of the Table 2-4 may need proper correction to substantiate the analytical results rather than reflecting the conditions described in the *Overview for the Technical Protocol for Natural Attenuation of Chlorinated Aliphatic Hydrocarbons in Groundwater* (Wiedemeier et al., 1996).

- Page 2-2, Area 1. It is stated that ground-water extraction efforts, which began in June 1996, do not seem to have affected the overall trends established before pumping began. Excluding an initial decrease at MW-5 in 1990, it is noted that this statement may not be substantiated by the data. Some inherent variability is expected to occur. For example, when different laboratories take, process, and analyze samples, variability will be introduced. It is noted that the earlier analytical results for sampling conducted in 1988 were reported by Groundwater Technology and the 1997 results by RUST.

  Once again (Figure 2-3), excluding the initial decrease in the concentrations of the COCs prior to 1991, a correlation between 1,1-DCA and the other COCs is not evident. However, the possible effect of the extraction effort on the overall decline in concentration of 1,1-DCA may not be ruled out. As depicted in Figure 2-4, the same trend may be evident for 1,1-DCA.

- Page 2-3, Area 3. Until a more in-depth evaluation of parent/daughter concentration ratios can be provided, the postulation of a summary statement that the reduction in concentration is due solely to the mechanisms of natural attenuation may be unwarranted.

- Page 2-4, Area 1. The document clearly claimed that the key VOCs at Area 1 are 1,1-DCA, 1,1,2-TCA, and chloroethane and added that as indicated in Figure

2-1, degradation of 1,1-DCA into chloroethane occurs primarily under anaerobic conditions. Are there any indications that anaerobic conditions are available at any of the monitoring locations?

- Page 2-5, 5th bullet. The highest dissolved organic carbon concentration occurred at RW-1 (7.3 mg/l) and the largest amount of CO_2 was recorded at RW-3 (423 mg/l). Production of the elevated CO_2 concentration in light of the reported dissolved oxygen content and organic carbon is questioned.

  An overall evaluation of data revealed that not only the readily available microbial sources of carbon and energy that are required for facilitating process of reductive dechlorination were absent, but also microbial metabolites (i.e., formic acid, acetic acid, propionic acid, butyric acid, lactic acid, malic acid, succinic acid) were devoid throughout the monitoring locations.

- Table 2-3. The lack of correlation between Eh and DO results is questioned. For example, Eh and DO results at MW-F are 158 mv and 10 mg/l while their values were 218 mv and 6.04 mg/l at the Chilcoat sampling location.

Parameters proposed for monitoring under the current Work Plan included:

Section 3.2.1 Groundwater Sampling: Ground water sampling will consist of ground water level measurements, well purging, field measurements (temperature, pH, dissolved oxygen, oxidation-reduction potential, and ferrous iron concentration).

Section 3.2.2 Analytical Testing Program: The analytical parameters for natural attenuation include VOCs, nitrate-nitrogen, total iron, sulfate, sulfide, chloride, carbon dioxide, alkalinity, ethane/ethene, heterotrophic plate count, phospholipid fatty acids, volatile fatty acids, dissolved organic carbon.

Except for the discussion relating to microbial analysis, it is our opinion that the listed indicators will represent the minimum required monitoring parameters needed to demonstrate that natural attenuation is occurring. With respect to the data set which would be required to demonstrate that the processes of natural attenuation are taking place and doing so at an acceptable rate, the number of samples will be determined by statistical correlations as discussed earlier.

In summary, the overall conditions seems to be aerobic which would favor biodegradation of vinyl chloride. However, under these conditions biodegradation of the more chlorinated solvents may not be substantial. This may be compounded by the low availability of the dissolved sources of carbon. Thus, the preponderance of the evidence presented at this site is ***not*** supportive of the substantial biodegradation activities. This is indicated by the lack of intermediate metabolites of aliphatic and aromatic hydrocarbons (volatile fatty acids), high oxygen content of the ground water, relatively low microbial population, low concentrations of dissolved organics required for the reductive dechlorination process, the absence of ethane and

ethene (except for minor concentrations of ethane at RW-3), and low methane content at this site. If you have any further questions concerning these comments please contact me at 580-436-8606.

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